

SOME ASPECTS OF TEM, SEM AND XRD INVESTIGATIONS OF VANADIUM PHOSPHORUS OXIDES

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Vanadium phosphorus oxides, (VPO) are commercially used as catalysts for the synthesis of maleic anhydride, (MA) for the partial oxidation of n-butane. Although these oxides have been studied for the last decade, still different phase components are announced in papers to play crucial role in the oxidation of n-butane. In the present work, some aspects of TEM, SEM and XRD investigations (peak overlapping, beam damage, multiplicity of phases, morphology) are presented.

Four samples were investigated: CAT60, prepared by reduction of V_2O_5 in a H_3PO_3 , H_2O , H_3PO_4 solution; CAT61, prepared as CAT60 but followed by reflux in H_2O ; CAT64, prepared by reduction of V_2O_4 in a H_2O and H_3PO_4 solution; and CAT65, prepared by reduction of V_2O_4 in a H_2O and $H_4P_2O_7$ solution. Samples were characterized by X-ray powder diffraction (on a Stoe Powder Diffractometer with the position sensitive detector), transmission electron microscope - operating in low magnification, high resolution imaging and diffraction mode (on Philips CM 200 FEG electron microscope) and scanning electron microscope (on Hitachi S-4000 SEM) for the information on morphology.

The powder XRD patterns for the four samples are shown in Fig. 1. The main reflections at ca. 23.0° , 28.3° and 29.6° 2θ can be assigned to the (020), (204) and (002) crystallographic planes of $(VO)_2P_2O_7$ (tetravalent phase). However, reflects due to pentavalent phases are found in the XRD patterns. The assignment of these additional peaks is rather complex due to the fact that three crystalline phases (α -, β -, γ - $VOPO_4$) exhibit reflections in the same region of investigation (table 1). Full and accurate phase characterization should be supported by ^{31}P NMR echo spin mapping measurements and laser Raman spectroscopy [1,2].

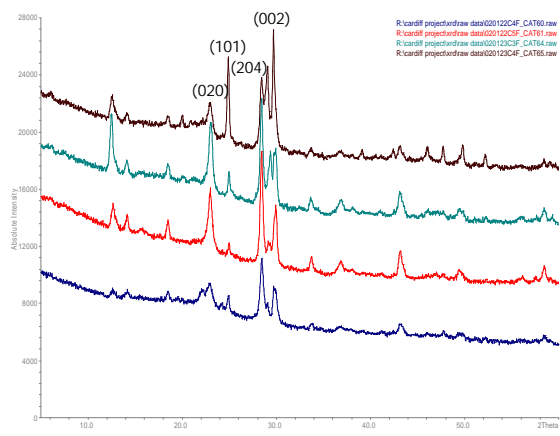


Fig. 1. XRD profiles for all samples

Table 1 – Phase identification in the region of 29° 2θ

2θ	phase	crystallographic plane
29,080	α - $VOPO_4$	(111)
29,082	β - $VOPO_4$	(020)
29,199	γ - $VOPO_4$	(311)

High resolution images (HREM) reveal that all four samples are very sensitive to the electron beam. Usually after a few seconds of irradiation, investigated region of the sample is damaged (changes in contrast, resulting in faint and diffuse lattice fringes). Typical images are reproduced in Fig. 2. Left image, (Fig. 2a) shows CAT64 sample before irradiation where lattice fringes are quite easily noticeable. Irradiation for 5 seconds (Fig. 2b) already produces changes in microstructure. Velocity of this process is determined by the type of the structure present in the compound (V^{4+} or V^{5+} phase), by the activation procedure (chemical or tribomechanical treatment) and also by the accelerating voltage of the microscope. HR images can be compared with simulated images of the VPO structures. After image processing by Fourier Transform, (FT) structure details can be estimated.

The micrographs from SEM (Fig. 3) reveal that the surface morphology of the investigated samples depends on the preparation routes. It ranges from thin and plate-like crystals (CAT60), to well-defined cubic crystallites with almost the same distribution within the limited range of investigation (CAT64). Quantitative elemental analysis exhibits very similar chemical constitutions for all catalysts.

Vanadium phosphorus oxides (V^{4+} and V^{5+}) can be distinguished between each other using a combination of different methods. But identification of phases must be supported by at least two independent techniques. More detailed results from XRD, TEM, SEM and image processing will be presented.

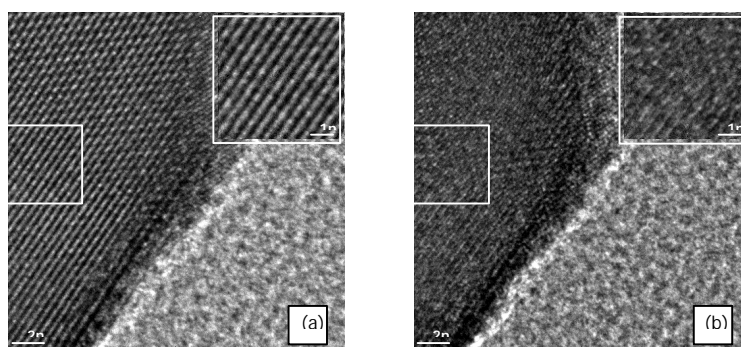


Fig. 2. HR images of CAT64, (a) before irradiation, (b) after 5 seconds

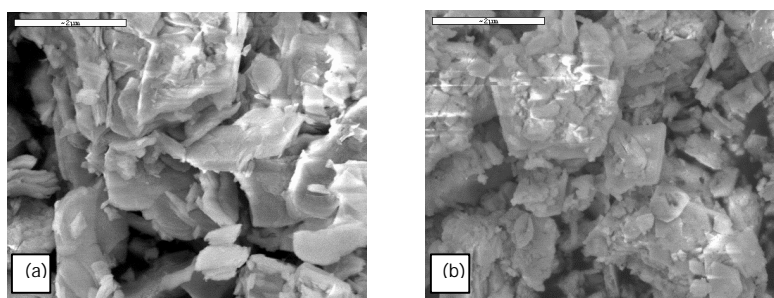


Fig. 3. SEM micrographs, (a) CAT60, (b) CAT64

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Reference:

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